PTO 99-5345

S.T.I.C. Translations Branch

(19) 日本国特許庁 (IP)

① 特許出願公開

⑩公開特許公報(A)

昭60-16419

௵Int. Cl.4

H 01 L 21/205 21/31 #H 01 L 33/00 庁内整理番号

7739—5 F 7739—5 F 6666—5 F ③公開 昭和60年(1985) 1 月28日

発明の数 1 審査請求 有

(全 5 頁)

⑤プラズマCVD処理装置

武蔵野市御殿山2-5-4日本

②特②出

願 昭58—124944

識別記号

願 昭58(1983)7月8日

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1. 発明の名称

プラズマCVD処理装置

2. 特許請求の範囲

(2) 前記気器容器の内面に沿ってガス傾射/ズルを形成し、 続ノズルと放射型材料との間に削足 熱電子陰極を設け、 続ノズルに向けて熱電子放電 を行なう特許温泉の範囲第1項記載のプラズマ C V D 処理装置。

- (3) 前記ノズルは環状であり、所望ガスと敏慢 成分とを含む混合ガスを順射する特許請求の範則 第2項記載のプラズマCVD処理發設。
- (4)前記熟證子絵様は複数個配置されている物 許請求の範囲第1項乃至は第3項の何れかに記載 のプラスマCVD類環装置。
- 3. 発明の詳細な説明

本発明は直設グロー放電により金属のハロゲン 化物や非化物をイオン化し、被処理材料表面に金 紙若しくは金属変化物、炭化物等の被額を生成す るプラズマCVD 処理接際に関する。

近野、食空魚着に比し、形成された競の代質が 非常に良いことからプラズマ中のイオンの無射を 利用して金 硫化合物等の成態を行なう、所謂 ノラスマ C V D 処理装置 (プラズマ中化学気相成長 装 引)が注目され、既に実用化の段略に入ろうとしている。

高波グロー放電を利用するアンズマCVD装置 においてはクロー放電のイオンの持つ運動エネル ギーによって放射型材料を展熱し、カ人ガスであ る整素ガス、水素ガス及び金属ハロゲン化合物若 しくは乳化物のガスをイオン化させることによっ て被処理材料表面に所建化合物のが緑を生成する ようしているが、金属分子のイオン化を高めるた めに平均電子温度をできるだけ高めることが必要 である。この半均電子温度Te は

上式より、平均電子器のTe はE/Pのパラメータに支配されているが、Eを入きくするには服 現があり、従来よりTe を大きくするために用力 Pを小さくすることが実行されている。

しかし、この様にしても直接グロー旅窓によるイメン化率は低く、高々数%に過ぎないので耐限の付置レートは非常に低い。プラズマCVDの場合、尋入ガス道はイオン化率若しくはプラズマ電力に依存しているため、付着レートを増大しよう

としてガス圧を高め、過剰ガスをお入すると未反応物が析出し、被収としては形成開発になる。 近って、ガス圧を低くすることは重要な設計であるが、ガス圧が低いとはグロー幅が広くなり、被処理材料コーナー部の付きまわりが悪くなると言う不具合が生する。

本発明は上記低来の欠点を解析し、プラズマCVD型理の被殴付着の迅速化を適り、場時間で均一にして充分な別さの被毀虧を形成し得るプラズマCVD型型装置を提供することを目的とするものである。

本先明の構成上の特徴は気能容器と、減気密容器内を前望の雰囲気にする手段と、減気器容器内に起設された被処理材料と、減放処理材料を放構に気器容器を開催にして政策圧を印加し設置が対して政策を提出させる政政区が認定と、前記被処理材料の表面に生成すべき段の成分を有するガスを訴訟に対する手段とを備えた状態にある。

料との中間の電圧を印制する意識電源を負債した プラズマCVO装置に存する。

以下図面に扱づき本発明を詳説する。

第1図は木発明の一実施例の構成略図、第2図 は第1図のA-A版面図であり、1は気管容器を 示している。装気密容器は排気管2を介して真空 ポンプ3に接続しており、内部が高真空に排気可 能である。前記気密容器は第2回から解るように 筒状をなしており、その中心部に電気導電性の被 処理材料ホルダー 4 が数裂されている。このホル ダーには名数の被処理材料 5 が積載されている。 前記ホルダー4は電気絶穀物を介して気密容器1 に取付けられており、直流路圧電源6の負端子に 接続されている。該高圧電源の正端子は気管容器 1 に接続され、アースされている。前記気密容器 の内面に接して環状のガスノズルフが同電位で設 けられ、容器外のガス導入源8より導入されたブ ラズマCVDに必要なガスが多数の微糊穴より容 窓の中心に向けて暗射される。前記ガス導入器の は体的構成を第3回に示してある。 向図中、9a. 9 b は ガスタンクであり、9 a に は 営 素 ガス が、 又 9 b に は 水 素 ガス が 封入 し て ある。 該 両 ガス タ ンク からの 配管の 途中に は 故 遊 額 整 割 1 0 e 。

15は前記被処型材料5とガスノズル7との間に配設された数制の熱電子除物であり、例えばタングステンのコイルで形成されている。 熱熱電子 気値は電気 乾燥 物を介して音器外に取出され、月上トランス16を介して交換 別熱電 数17に接続されている。前記列圧トランスの2次 例中程度は

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特問昭60-16419(3)

直数信報 1 8 の負端子に接続され、気密音器及び ガスノズルに対して負の電位に保持される。第 4 図はガスノズルで、熱電子接接 1 5、被処理材料 5のポテンシャルを示してあり、熱電子接接は一 1 2 0 V に、被処理材料 5 は - 5 2 0 V に保持されている。

上記構成の装置の動作を次ぎに説明する。

機需報18より電子加速電圧を印加すると該然電子監修からの電子は該院権よりプラス電気のガスノズル7に向けて限期する(熱院権グロー級電と言う)。前記熱電子監視15と気管管器1との間の電圧は第4位に示すように例えば120V程度であり、被処理材料5と容器1との間の主グロー級電圧を立してある。

建材料に引付けられる。前記熱陰様グロー放電は 被処理材料温度に直接関与しないので、あまり制 限されることなく放電電力を高めることが可能で める。そのため、主グロー放電のみの場合より気 倍育器内の金属ガスのイオン化が総体的に増大し、 その分ガス圧を高めることができ、金属イオン数 が増大し、初製付着レートを著しく増大すること ができる。

次に実験例について説明する。

[1] 従来の装置による実験例

ガス混合比 N 2 = 30% . H 2 = 60% .

Ticl . = 10% 600 °C

划型温度

処理ガス圧 1 Torr

主グロー電圧 600 V

付着レート 120 A/min

砂処理ガス圧をこれ以上高くすると未反応物が折出し、放膜を形成することができなくなる。

【2】 木発明装置による実験例

ガス混合比 N2 = 30% . H2 = 50% .

Ticl 4 = 10%

処理温度 600 ℃

処理ガス圧 4 Torr主クロー電圧 5 2 0 V

然電子陰極温度 2200 °C

以上の海実験例から解るように、木茂明によればガス圧を高めることが可能であり、その結果付

省レートを従来の約3倍に崩大することができ、 金殿化合物級膜の迅速な生成が可能となる。

高、上記は本発明の一実施例であり実用に当っては極々な変更が可能である。例えば、急騰板は 第1回、第2 図に示すような構造に限られず、行 勿な熱験板グロー放電が可能であればどの延な の のでも良く、第5 図の様の信な情報の続 株で がても良い。又、実験例に使用したガス产金配ガ スの優類、各様の動物はこれに限定されるしので

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4. 図面の簡単な説明

第1回は本発明の一実施保を示す保成監督、第 2回は第1回接置のA-A 知断値図、第3回は第 1回装置の一部員体例を示す例、第4回は第1回 装置の主要部の電位勾配を示す例、第4回は第1 回装置の一部の他の例を示す図である。

1 -- 気管容器

3…真空ポンプ

4 … ホルダー

5 … 被処理材料

6 … 直旋高压能源

7…ガスノズル

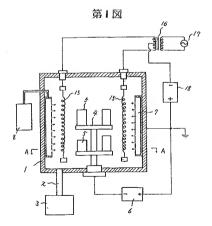
8 … ガス殺入欲

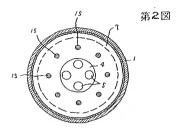
15…然電子陰極

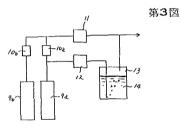
16 … 昇圧トランス

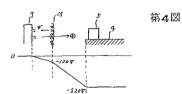
17…加熱電源

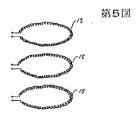
18… 直級電腦











JA 016419

(54) PLASMA CVD PROCESSING APPARATUS

(11) 60-16419 (A)

(21) Appl. No. 58-124944

(43) 28.1.1985 (19) JP (22) 8.7.1983

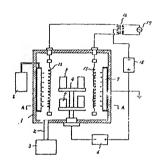
(71) NIHON DENSHI KOGYO K.K. (72) TADASHI MATSUZAWA

(51) Int. CF. H01L21/205,H01L21/31//H01L33/00

PURPOSE: To obtain a film in the sufficient thickness within a short period of time by putting a material to be processed into a hermetically sealed reservoir and supplying a film forming gas, generating DC plasma between the cathode made of a material to be processed and the anode made of reservoir, providing a hot electron cathode between the reservoir and material at the time of generating the desired film on the surface of material and by applying an inter-

mediate voltage thereto.

CONSTITUTION: A multi-stage holder 4 is provided in a cylindrical sealed reservoir 1, many conductive material to be processed 5 are placed thereon, and a ring-shaped gas nozzle 7 is provided to the internal circumference of reservoir 1 while it is kept at the same potential as the reservoir 1. The reservoir 1 is vacuumed by an exhaust pipe 2 connected to a vacuum pump 3 and a raw gas for filming is sent thereto from a gas source 8. Thereafter, the negative terminal of external DC voltage source 6 is connected to the holder, namely to the material 5 and the positive terminal is connected to the reservoir 1 and is grounded. Moreover, a coiled hot electron cathode 15 is provided vertically between the nozzle 7 and material and an intermediate voltage sent from the AC heating power supply 17 through a boosting transformer 16 is applied to said cathode.



PTO 99-5345

CY=JP DATE=19850128 KIND=A PN=60016419

PLASMA CVD PROCESSING APPARATUS [Purazuma CVD shori sochi]

Tadashi Matsuzawa

UNITED STATES PATENT AND TRADEMARK OFFICE Washington, D.C. September 1999

Translated by: Diplomatic Language Services, Inc.

PUBLICATION COUNTRY (19): JP

DOCUMENT NUMBER (11): 60016419

DOCUMENT KIND (12): A (13):

PUBLICATION DATE (43): 19850128

PUBLICATION DATE (45):

APPLICATION NUMBER (21): 58124944

APPLICATION DATE (22): 19830708

ADDITION TO (61):

INTERNATIONAL CLASSIFICATION (51): H01L 21/205; 21/31; //H01L 33/00

DOMESTIC CLASSIFICATION (52):

PRIORITY COUNTRY (33):

PRIORITY NUMBER (31):

PRIORITY DATE (32):

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TITLE (54): PLASMA CVD PROCESSING APPARATUS

FOREIGN TITLE [54A]: PURAZUMA CVD SHORI SOCHI

Specification

Title of the Invention
 Plasma CVD processing apparatus

2. Claims

- (1) A plasma CVD processing apparatus having a gas-tight vessel, a means for making the inside of that gas-tight vessel into a desired atmosphere, a processed material placed inside that gas-tight vessel, a DC high-voltage power supply that applies high-voltage electricity with that processed material as cathode and the gas-tight vessel as anode and generates a DC plasma, and a means for introducing a gas having constituents of a film to be formed on the surface of said processed material into said gas-tight vessel, wherein a hot electron cathode is provided between said gas-tight vessel and processed material, and there is furnished a DC power supply for applying to that hot electron cathode intermediate voltage between the gas-tight vessel and the processed material.
- (2) A plasma CVD processing apparatus as defined in Claim 1, wherein a gas spraying nozzle is formed following the inner surface of said gas-tight vessel, said hot electron cathode is provided between that nozzle and the processed material, and a hot electron discharge is made toward that nozzle.
- (3) A plasma CVD processing apparatus as defined in Claim 2, wherein said nozzle is ring-shaped, and it sprays mixed gas containing a desired gas and film constituents.

(4) A plasma CVD processing apparatus as defined in any of Claim 1 through Claim 3, wherein said hot electron cathode is placed as a plurality.

3. Detailed Explanation of the Invention

The present invention relates to a plasma CVD processing apparatus that ionizes a halogen compound or fluoride compound of a metal by direct current glow discharge and generates a film of metal or metal nitride, carbide, and the like on the surface of a processed material.

In recent times, so-called plasma CVD processing apparatuses (apparatuses for chemical gas-phase deposition in plasma), which perform deposition of films of metal compounds and the like by using irradiation of ions in a plasma, have attracted attention since the quality of the deposited films is very good compared with vacuum deposition, and they are already starting to enter into the stage of practical use.

In a plasma CVD apparatus using direct current glow discharge, the processed material is heated by kinetic energy having ions of the glow discharge, and a thin film of a desired compound is formed on the surface of the processed material by ionizing the introduced gas, being nitrogen gas, hydrogen gas, and a halogen compound or fluoride compound of metal, but in order to increase the ionization of the metal molecules, the average electron temperature must be raised as much as possible. This average electron temperature is represented by:

Te =
$$q / k 0.3 \sqrt{Mm} / Me \lambda e E / P$$

Here, q is the electron charge, k is the Boltzmann constant, Mm and Me are respectively the mass of the gas molecules and the electrons, λe is

a free process of electrons at $0^{\circ}C$ and 1 Torr, E is the electric field strength, and P is the pressure.

By the above formula, the average electron temperature Te is governed by the E / P parameter, but there is a limit to making E larger, and from the past, pressure P was made smaller in order to make Te larger.

However, even when doing thus, the ionization rate by direct current glow discharge is low and does not exceed as much as several %, therefore the adhesion rate of thin film is very low. In the case of plasma CVD, because the quantity of introduced gas is dependent on the ionization rate or plasma power, when the gas pressure is raised and excess gas is introduced in the attempt to increase the adhesion rate, unreacted substances are deposited, and it is difficult to form as a film. Accordingly, it is an important condition that the gas pressure be lowered, but when the gas pressure is low, it is inconvenient that the negative glow width becomes wider, and the vicinity of the corner parts of the processed material becomes poor.

The present invention aims to provide a plasma CVD processing apparatus that solves the abovementioned problems of the past, attempts acceleration of the adhesion of film in plasma CVD processing, and can form a uniform film layer of sufficient thickness in a short time.

The constitutive characteristics of the present invention are in a plasma CVD processing apparatus having a gas-tight vessel, a means for making the inside of that gas-tight vessel into a desired atmosphere, a processed material placed inside that gas-tight vessel, a DC high-voltage power supply that applies high-voltage electricity with that

processed material as cathode and the gas-tight vessel as anode and generates a DC plasma, and a means for introducing a gas having constituents of a film to be formed on the surface of said processed material into said gas-tight vessel, wherein a hot electron cathode is provided between said gas-tight vessel and processed material, and there is furnished a DC power supply for applying to that hot electron cathode intermediate voltage between the gas-tight vessel and the processed material.

The present invention is explained in detail below based on drawings.

Figure 1 is a component diagram of one working example of the present invention, and Figure 2 is a sectional view in the A-A line of Figure 1. 1 indicates a gas-tight vessel. That gas-tight vessel is connected to a vacuum pump 3 by way of an exhaust pipe 2, and the inside is capable of being drawn to a high vacuum. Said gas-tight vessel is cylindrically shaped as is clear from Figure 2, and an electrically conductive processed material holder 4 is placed in the center part thereof. This holder has a large number of processed materials 5 stacked on it. Said holder 4 is connected to gas-tight vessel 1 by way of an electrically insulating material, and the negative terminal of a DC high-voltage power supply 6 is connected to it. The positive terminal of that high-voltage power supply is connected to gas-tight vessel 1, and it is grounded. A ring-shaped gas nozzle 7 is provided in contact with the inner surface of said gas-tight vessel and at the same potential, and gas necessary for plasma CVD being introduced from a gas introduction source 8 outside the vessel is sprayed toward the center of

the vessel through a large number of fine holes. A specific configuration of said gas introduction source is shown in Figure 3. In the same drawing, 9a and 9b are gas tanks, and 9a is filled with nitrogen gas and 9b with hydrogen gas. Mid-course of piping from both of those gas tanks, there are provided flow regulators 10a and 10b, and the mixture ratio of both gases can be regulated. The gases coming out of both regulators are mixed and are supplied to gas-tight vessel 1 by way of flow regulator 11. Meanwhile, from nitrogen gas tank 9a, nitrogen gas is introduced into a bubbling vessel 13 by way of flow regulator 12, a liquid alloy 14 inside that vessel, such as TiCl₄, is gasified by that gas, it is mixed with said mixed gas of nitrogen and hydrogen, and it is introduced into gas nozzle 7 inside gas-tight vessel 1. The manner of the bubbling vessel is not limited to the abovementioned, and it may be one combining heating or one that mainly performs heating.

15 is a plurality of hot electron cathodes disposed between said processed material 5 and gas nozzle 7, and it is formed, for example, with a tungsten coil. That hot electron cathode is led out from the vessel by way of an electrically insulating material, and it is connected to an AC heating power supply 17 by way of a boosting transistor 16. The neutral point on the secondary side of said boosting transistor is connected to the negative terminal of a DC power supply 18, and it is kept to negative potential with respect to the gas-tight vessel and the gas nozzle. Figure 4 shows the potential of gas nozzle 7, hot electron cathode 15, and processed material 5, and the hot electron cathode is kept to -120 V and processed material 5 to -520 V.

The operation of the apparatus of the abovementioned configuration

is explained next.

Processed materials 5 are stacked on top of holder 4 inside gastight vessel 1, and the inside of that gas-tight vessel is exhausted by vacuum pump 3. After that, the mixture ratio of nitrogen gas, hydrogen gas, and liquid metal gas is regulated by adjusting each flow regulator 10a, 10b, 11, 12 of gas introduction source 8 shown in Figure 3, and they are introduced into gas-tight vessel 1. Doing thus, the inside of the vessel is made into a gas atmosphere of the desired pressure $(10^{-1}$ -20 Torr). In this state, 200 V - several KV of voltage is applied between vessel 1 and processed material 5 from DC high-voltage power supply 6, and a DC glow discharge (main glow discharge) is generated inside the vessel. At the same time, when heating current is supplied to hot electron cathode 15 from power supply 17 such that it is heated to a temperature to the extent that generation of hot electrons is possible, and electron accelerating voltage is applied from DC power supply 18, electrons from that hot electron cathode leap from that cathode toward gas nozzle 7 having plus potential (called hot cathode glow discharge). The voltage between said hot electron cathode 15 and gas-tight vessel 1 is about 120 V, for example, as shown in Figure 4, and it is a sufficiently low voltage compared with the voltage, such as 520 V, generated by the main glow discharge between processed material 5 and vessel 1.

The ions generated by said main glow discharge are accelerated by the electrical field between vessel 1 and processed material 5, and they collide with that material and heat that material. Also, the metal ions generated in the main glow discharge are attracted to the processed

material, and they adhere as they are or adhere as a metal compound reacting with other ions. The rate of thin film adhesion by such main glow discharge is very low as discussed before, but in the present invention, because a hot cathode glow discharge using hot electron cathode 15 is generated separately from the main glow discharge, a large volume of ions is generated between the hot electron cathode and the gas nozzle in addition to the generation of ions by said main glow discharge, and those ions are attracted to the processed material. Because the aforementioned hot cathode glow discharge does not directly contribute to the temperature of the processed material, it is possible to raise the discharge power without being constrained so much. Therefore, the ionization of the metal gas inside the gas-tight vessel is increased on the whole more so than just by the main glow discharge and the gas pressure can be raised by that much, and the number of metal ions is increased and the thin film adhesion rate can be markedly increased.

Next, working examples are explained.

[1] Working example with apparatus of the past

Gas mixture ratio	$N_2 = 30\%$, $H_2 = 60\%$, $TiCl_4 = 10\%$
Processing temperature	600°C
Processing gas pressure	1 Torr
Main glow voltage	600 V
Adhesion rate	120 Å/min

* If processing gas pressure is made higher than this, unreacted substances are deposited, and a film can no longer be formed. [2] Working example with apparatus of the present invention

Gas mixture ratio $N_2 = 30\%$, $H_2 = 60\%$, $TiCl_4 = 10\%$ Processing temperature $600^{\circ}C$ Processing gas pressure 4 Torr

Main glow voltage 520 V

Hot electron cathode temperature $2200^{\circ}C$ Hot cathode glow voltage 120 V

Adhesion rate 300 Å/min

As is clear from the above quantities, according to the present invention, it is possible to raise the gas pressure, and as a result, the adhesion rate can be increased to about 3 times that of the past, and fast formation of films of metal compounds becomes possible.

The abovementioned is one working example of the present invention, and various modifications are possible in practical use. For example, the hot cathode is not limited to the structure as shown in Figure 1 and Figure 2, it can be any kind of thing as long as an effective hot cathode glow discharge is possible, and a plurality of wheel-shaped cathodes as shown in Figure 5 may also be provided. Also, the types of gases and metal gases and the values of each type used in the working example are not limited to these.

4. Brief Explanation of the Figures

Figure 1 is a component diagram showing one working example of the present invention, Figure 2 is a sectional view in the A-A line of the apparatus in Figure 1, Figure 3 is a drawing showing a specific example of a part of the apparatus in Figure 1, Figure 4 is a drawing showing

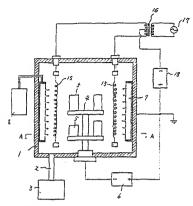


Figure 1

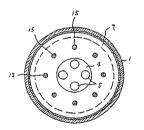


Figure 2

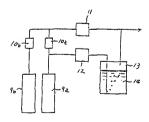


Figure 3

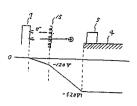


Figure 4



Figure 5